WATER RESOURCES RESEARCH GRANT PROPOSAL

Project ID: MA2301

Title: Sources and behavior of copper-binding compounds in rivers and estuaries

Focus Categories: Toxic Substances, Surface Water

Keywords: humic substances, dissolved organic matter, complexation, copper

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Federal Funds: $24,291

Non-Federal Matching Funds: $61,628

Congressional District: Eighth Congressional District of Massachusetts

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Abstract

Statement of critical regional or State water problem: Concentrations of copper in effluents from publicly-owned treatment works and other dischargers in Massachusetts regularly exceed permitted levels. It is generally agreed that current water quality criteria for copper, based on laboratory toxicity tests, are often stricter than intended by regulatory guidelines. The main reason for this is that complexation (binding) of copper by naturally present dissolved organic compounds decreases bioavailability of copper, resulting in lower toxicity in the natural waters than would be observed in the laboratory tests. Conducting toxicity tests in individual receiving waters to develop site-specific water quality criteria is possible, but prohibitively expensive. The U.S. Environmental Protection Agency (EPA) Office of Water has therefore supported the development of a chemical-biological model predicting copper toxicity in a given water as a function of easily measurable chemical parameters including pH, concentration of dissolved organic carbon, and concentrations of major ions such as calcium, magnesium, and sulfate. The EPA, the Massachusetts Department of Environmental Protection (MADEP) and other states' regulatory agencies, as well as the region's dischargers, are all interested in the speedy validation of this "Biotic Ligand Model" as a low-cost technique for developing site-specific water quality criteria for copper.

The Biotic Ligand Model's ability to produce accurate predictions of copper toxicity in an effluent-receiving water depends on its ability to predict the extent of copper complexation in that water. The model assumes that humic substances, the biologically refractory degradation products of higher plants, are both the copper-binding compounds controlling complexation and the main constituents of the dissolved organic carbon present in surface waters. However, other compounds less abundant than humic substances have been shown to be more significant copper complexing agents in a variety of natural waters. In addition, other organic compounds may constitute a significant fraction of the dissolved organic carbon, especially in estuaries and sewage effluents. The assumptions of the Biotic Ligand Model may therefore lead to both overestimates or underestimates of the actual toxicity of copper in a given water. The goal of the study proposed here is to examine the behavior of copper-binding compounds in a sewage-effluent impacted river and in a relatively unimpacted estuary in order to determine whether the assumptions made by the Biotic Ligand Model lead to reasonable predictions of copper toxicity in these systems or whether other factors need to be taken into account.

Statement of expected results or benefits: In the first part of the proposed study, we plan to collaborate closely with an ongoing project in the Taunton River watershed in Massachusetts, whose goals are to validate the Biotic Ligand Model using concurrent toxicity studies, and, if the validation is successful, to apply the model to the development of site-specific water quality criteria for copper. The project is being conducted by the consulting firm ENSR (Acton, MA) under the auspices of the MADEP and the EPA Region I office. This project is one of the first of its kind to be conducted not only in the region but nationwide. If the proposed work is funded, our participation will provide valuable additional information to this study. If the results of ENSR's toxicity tests are found to differ from predictions made by the Biotic Ligand Model, our direct measurements of copper complexation will indicate whether the reason for the model's failure lies in the chemical part of the model, that is, the prediction of copper binding by dissolved organic matter, or in the biological part, which predicts the toxicity of the uncomplexed fraction of the copper in the sample. Our measurements may also be used in lieu of the chemical model, if the latter should turn out to be problematic in some waters. In addition, our study will address whether qualitative differences exist in dissolved organic matter from different sources, for example sewage versus rivers, which will need to be taken into account in future refinements of the mo del.

The goal of the second part of the proposed study is to examine the behavior of copper-binding compounds from riverine sources as they enter an estuary. Do humic substances remain the dominant player in the copper-binding properties of the river water as it mixes with seawater? Do they remain the major constituent of dissolved organic carbon? If the answer to either of these questions is negative, the Biotic Ligand Model as currently formulated will not provide accurate predictions of copper toxicity in estuarine systems. In this case, as in the case of effluent-impacted rivers, our studies of sources and behavior of copper-binding compounds can be used to evaluate under which conditions the Biotic Ligand Model is likely to produce valid results, and may suggest refinements of the model to expand its usefulness.